

# PATENT SPECIFICATION

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## (54) COATING PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the application of protective and decorative coatings to surfaces, particularly the surfaces of automobile bodies.

It is well known to employ, especially in the automobile industry, coating compositions which contain metallic pigments; these are the so-called "glamour metallic" finishes whereby a differential light reflection effect, depending on the viewing angle, is achieved. To maximise this "flip" tone effect, careful formulation of the coating composition in regard both to the film-forming resin and to the liquid medium is required. Difficulties may be encountered in meeting this objective and at the same time achieving a high degree of gloss in the final finish such as is usually desired in the automobile field. For this reason, one of the procedures which has been proposed for producing metallic finishes in a two-coat procedure, in which there is first applied to the surface of the substrate a base-coat containing the metallic pigment and formulated so as to give the optimum "flip" effect, and there is then applied over the base-coat an unpigmented top-coat which will yield the desired degree of gloss without in any way modifying the characteristics of the base-coat.

An essential feature of a successful two-coat metallic finish system is that there must be no tendency for the top-coat, when applied, to mix with, or even have any appreciable solvent action on, the previously applied base-

coat. If this requirement is not fulfilled, the metallic pigmentation effect may be seriously impaired. One way of meeting the requirement is to arrange for the base-coat to be of the thermosetting type and to give that coat at least a short curing treatment before the top-coat is applied, but this introduces an undesirable complication into the production schedule by interrupting the spraying operation with a stoving operation. A more desirable state of affairs is that the base-coat should be capable of drying in a few minutes only, under normal spray-booth conditions, to an extent such that it is not disturbed by the application to it of the top-coat.

For two-coat automobile metallic finishes based on solution of acrylic polymers in volatile organic solvents, one method which has been proposed in order to achieve the last-mentioned objective is to employ as the base-coat a pigmented solution of an acrylic polymer containing a cellulose ester, for example cellulose acetate butyrate, and as the top-coat an unpigmented solution of a specified cross-linkable acrylic copolymer together with a cross-linking agent for the copolymer; the base-coat is applied to the substrate and the top-coat is subsequently applied without any intermediate baking of the base-coat, a final stoving operation being given to cure the top-coat.

It has now been found that a useful improvement over this known process can be achieved if the top-coat, instead of being formulated with a solution of an acrylic polymer, is based on a dispersion of specified type of an acrylic polymer in a non-solvent organic liquid.

According to the present invention there is provided a process for the application to a substrate surface of a protective and decorative coating which comprises the steps of (i)

applying to the surface a base-coat composition comprising a film-forming, optionally thermosetting, acrylic polymer as hereinafter defined and a cellulose ester both carried in a volatile organic liquid, the cellulose ester constituting from 2% to 70% of the combined weight of the acrylic polymer and the cellulose ester, together with one or more pigments and optionally a heat-curable cross-linking agent for the base-coat polymer, (ii) drying the base-coat so applied without any stoving operation, to a degree sufficient to permit application thereto of the below-described top-coat composition with substantially no intermixing, (iii) applying to the dried base-coat an unpigmented top-coat composition comprising a stable dispersion of a thermosetting acrylic polymer as hereinafter defined in a volatile organic liquid in which the polymer is insoluble, together with a heat-curable cross-linking agent for the thermosetting polymer, the dispersion being stabilised by means of a copolymer stabiliser containing one polymeric constituent which is capable of becoming associated with the polymer particles and can additionally become covalently linked to the said polymer, and another polymeric constituent of different polarity which is solvatable by the organic liquid medium, and (iv) subjecting the substrate with the applied base-coat and top-coat to heat in order to cure the unpigmented top-coat and, as appropriate, also the base-coat.

The cellulose ester used in the formulation of the base-coat composition may be, for example, cellulose nitrate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate or cellulose acetate propionate, or a mixture of these esters. The preferred cellulose ester is, however, cellulose acetate butyrate, in particular grades thereof having a viscosity of from 0.1 to 25 seconds as determined by ASTM Method D-1343-69.

The cellulose ester preferably constitutes from 20% to 50% of the combined weight of the cellulose ester and the acrylic polymer in the base-coat composition.

The pigments which are of particular interest as constituents of the base-coat composition are metallic pigments such as aluminium flake or copper bronze flake, but other pigments, both organic and inorganic, commonly employed in coating compositions may be used either alternatively or additionally, for example red and yellow iron oxides, metal chromates, phthalocyanine blue, phthalocyanine green, dioxazine violet, mineral carbon black and vegetable carbon black. The pigment particles can in general range in size from  $1\ \mu$  to  $50\ \mu$ ; the so-called "transparent" iron oxide pigments, which are very suitable for use according to the invention, usually have particle sizes in the region of  $1\ \mu$ .

By "acrylic polymer" is meant herein a polymer or copolymer of one or more alkyl

esters of acrylic or methacrylic acids, optionally together with other ethylenically unsaturated monomers such as vinyl acetate, acrylonitrile or styrene. The base-coat acrylic polymer may be of either the thermoplastic type or, like the top-coat polymer, of the thermosetting type. Cross-linking, thermosetting type base-coat polymers are, however, strongly preferred for use according to the invention. Suitable acrylic esters for either type of polymer include methyl methacrylate, butyl methacrylate, ethyl acrylate and 2-ethylhexyl acrylate. Where the polymer is required to be of the cross-linking type, suitable functional monomers to be used in addition to the above include acrylic acid, methacrylic acid, hydroxyethyl methacrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate, and the base-coat composition will in such a case contain also a cross-linking agent such as a melamine-formaldehyde resin, and optionally a catalyst for the cross-linking reaction, as discussed in more detail below in connection with the top-coat compositions.

The base-coat composition may, according to one embodiment of the present invention, contain the acrylic polymer in a state of stable dispersion in the organic liquid medium of the composition, which in this case will be a non-solvent for the polymer. Methods of preparing such acrylic polymer dispersions are fully described in the patent and other literature, to which further reference is made below in connection with the top-coat compositions. In such case, although the acrylic polymer is not in solution in the liquid medium of the composition, the cellulose ester will normally be dissolved by that medium. It will usually be most convenient to blend the cellulose ester, previously dissolved in a suitable solvent such as butyl acetate, to the already-prepared acrylic polymer dispersion. The same mode of addition will apply to any cross-linking agent which is incorporated in a dispersion-type base-coat composition.

The base-coat composition may contain, in addition to film-forming polymer which is in a state of dispersion in the organic liquid medium, supplementary acrylic polymer which is in solution in that medium. This aspect is discussed further below, in connection with top-coat compositions for use according to the invention.

According to another embodiment of the invention, the acrylic polymer is present in the base-coat composition wholly in a state of solution in the organic liquid medium. In this case the acrylic polymer may be prepared by solution polymerisation of the monomer(s), in the presence of suitable catalysts or initiators such as organic peroxides or azodiisobutyronitrile, in the organic liquid medium itself, and the other constituents (i.e. the cellulose ester and the cross-linking agent, if any) may

then be dissolved in the resulting polymer solution. Alternatively the acrylic polymer may be prepared in a separate previous operation (e.g. by aqueous emulsion polymerisation techniques) and dissolved in the organic liquid medium along with the other constituents.

Whether the base-coat is formulated with a polymer in dispersion or in solution, the incorporation of metallic or other pigments may be carried out using the methods well established in the coatings art. Preferably the pigment is added as a pre-formed millbase.

Volatile organic liquids which may be used in formulating the base-coat composition include those conventionally used in coating compositions, for example aliphatic and aromatic hydrocarbons such as petroleum spirit, toluene and xylene, esters such as butyl acetate, ketones such as acetone and methyl isobutyl ketone, and alcohols such as butyl alcohol. The actual liquid or mixture of liquids selected will depend upon the nature of the acrylic polymer used and whether the polymer is present in the composition as a dispersion or as a solution.

The acrylic polymer employed in the top-coat composition may be any conventional polymer or copolymer of one or more alkyl esters of acrylic or methacrylic acid, optionally together with other ethylenically unsaturated monomers, as described above in connection with the base-coats. The top-coat polymer is, however, specifically a thermosetting polymer and it will therefore include units derived from monomers containing functional groups, such as acrylic or methacrylic acids and the hydroxyalkyl esters of those acids previously mentioned.

It is also an essential feature of the invention that the acrylic polymer is present in the top-coat composition in a state of stable dispersion in the organic liquid medium employed (i.e. the polymer is insoluble in that liquid). According to the invention the disperse polymer is stabilised by means of a copolymer stabiliser containing one polymeric constituent which is capable of becoming associated with the polymer particles and can additionally become covalently linked to the said polymer, and another polymeric constituent of different polarity which is solvatable by the organic liquid of the dispersion and so provides a stabilising steric sheath around the particles. This mode of stabilisation is described in British Patent Specification No. 1,231,614 and is a development of the known art concerning suitable stabilisers and methods of making stable dispersions of acrylic polymers, as extensively described in the patent literature, for example in British Patent Specifications Nos. 941,305, 1,052,241, 1,122,397, 1,123,611 and 1,143,404. A preferred procedure, based on what is described in these specifications, is that of polymerising the monomer or monomers, from which the

acrylic polymer is to be derived, in an inert organic liquid in which the monomers are soluble but in which the resulting polymer is insoluble, in the presence of a polymeric stabiliser of the type described above. The inert organic liquid employed in the actual production of the polymer dispersion need not necessarily be the sole organic liquid present in the complete top-coat composition; certain constituents of the organic liquid of the total composition may be added after formation of the dispersion, and these may include regulated amounts of liquids which are solvents for the polymer, as described in the complete specification filed in pursuance of British Applications Nos. 58995/71 and 8863/72 (Serial No. 1,409,719). However, the organic liquid of the total composition must, as a whole, be a non-solvent for the polymer.

The cross-linking agent used in the top-coat composition, and also, where appropriate, in the base-coat composition, may be, for example, a diisocyanate or an epoxide; more usually, however, it will be an aminoplast resin, that is to say a condensate of formaldehyde with a nitrogenous compound such as urea, melamine or thiourea, or a lower alkyl ether of such a condensate. Especially suitable are melamine-formaldehyde condensates in which a substantial proportion of the methylol groups are etherified by reaction with butanol.

The proportion of cross-linking agent to cross-linkable acrylic polymer in the top-coat or base-coat composition may vary widely, but in general a ratio of from 50:50 to 90:10 by weight of acrylic polymer to cross-linking agent is satisfactory. The precise proportion to be employed, particularly in the top-coat composition, depends upon the properties required in the final film, but a preferred range affording a good balance of properties is from 60:40 to 85:15 by weight of acrylic polymer to cross-linking agent. Where it is of particular importance that the top-coat film should exhibit good resistance towards acid corrosion induced by severe atmospheric pollution, an especially preferred range of ratios of acrylic polymer to cross-linking agent is from 70:30 to 85:15 by weight.

The top-coat composition and, where it is of the thermosetting type, the base-coat composition also, may incorporate a suitable catalyst for the cross-linking reaction, for example an acid-reacting compound such as acid butyl maleate, acid butyl phosphate or *p*-toluene sulphonic acid. Alternatively the acrylic polymer of the composition may be arranged to contain free acid groups, as for example by the incorporation in it of units derived from acrylic or methacrylic acids.

The top-coat composition may contain, in addition to the main disperse film-forming polymer, which is, of course, insoluble in the organic liquid medium of the composition,

supplementary film-forming polymer which is in solution in that medium. This supplementary polymer may be an acrylic polymer which is formed simultaneously with the disperse polymer during polymerisation of the monomers; or it may be an added, preformed polymer which, unlike the disperse polymer, is soluble in the organic liquid in which the dispersion is produced. Again, it may be a polymer which is insoluble in the organic liquid in which the main polymer dispersion is produced and is initially also in dispersion therein but which passes into solution on the subsequent addition to that liquid of certain further liquid constituents of the total composition, as already described; yet again, it may be an added, preformed polymer which is soluble in the organic liquid of the total composition although insoluble in the organic liquid in which the main polymer dispersion is produced. The amount of the supplementary, soluble polymer present in the top-coat composition may be comparable with, or may even substantially exceed, the amount of the insoluble disperse polymer present without departing from the scope and advantages of the present invention.

The description in the previous paragraph applies equally to the optional presence in a dispersion-type base-coat composition of soluble supplementary polymer. In this instance, such polymer may result, for example, from the introduction into the polymer dispersion of a relatively strong solvent, such as butylacetate, in which the cellulose ester is dissolved, as already mentioned.

Volatile organic liquids suitable for incorporation in the top-coat composition include those organic liquids mentioned above in connection with the base-coat, although in practice, because of the fact that the liquid is required to be as a whole a non-solvent for the acrylic polymer present in dispersion form, liquids of relatively low polarity such as aliphatic and aromatic hydrocarbons will tend to predominate in the top-coat medium.

In the first operational step of the process of the invention, the base-coat composition is applied to the surface of the substrate, which may be previously primed or otherwise treated as conventional in the art. The substrates which are of principal interest in the context of the invention are metals such as steel or aluminium which are commonly used for the fabrication of automobile bodies, but other materials such as glass, ceramics, wood and even plastics can be used provided they are capable of withstanding the temperatures at which final curing of the coating is effected. After application, the base-coat is allowed to dry under ambient conditions for a short period before the top-coat is applied. It is a particular feature of the invention that the formulation of the base-coat and top-coat respectively require only a short period of dry-

ing of the base-coat, of the order of 1—10 minutes at a temperature of 15—35°C, in order that the top-coat can be applied thereto without there being any tendency for the latter to mix with or dissolve the base-coat film in a way which could alter the disposition of pigments in the base-coat, particularly the orientation of metallic flake. At the same time the base-coat is adequately wetted by the top-coat so as to ensure satisfactory inter-coat adhesion.

Without in any way proposing to restrict by reference to a conjectured mechanism of its operation, we believe that the achievement of the above-mentioned characteristics may be attributed both to the incorporation of the cellulose ester with the acrylic polymer in the base-coat and to the use as the top-coat of an acrylic polymer in a state of dispersion in an organic liquid which is of low polarity relative to that of both the polymers involved. The successful performance of the invention may be further assisted if the acrylic polymer of the base-coat is of a composition of somewhat higher polarity than that of the top-coat polymer, so that any tendency for the liquid medium of the top-coat to dissolve the base-coat polymer is further diminished, and this condition is more readily met if the base-coat polymer is present in a state of solution, rather than of dispersion, in the liquid medium of the base-coat.

After application of the top-coat composition to the base-coat film, the coated substrate is subjected to a curing operation in which the top-coat, and, in the preferred embodiment of the invention, the base-coat also, is cross-linked with the aid of the cross-linking agent(s) present. This curing operation is carried out at an elevated temperature as conventional in the thermosetting coating composition art, usually at a temperature in the range 100—140°C but, if desired, at a lower temperature provided the cross-linking system is sufficiently reactive.

In performing the process of the invention, the base-coat and top-coat compositions may be applied to the substrate by any of the conventional techniques such as brushing, spraying, dipping or flowing, but is preferred that spray application be used since the best results are thereby achieved in regard to both pigment control, especially of metallic pigment orientation, and gloss. Any of the known spray procedures may be adopted, such as compressed air spraying, electrostatic spraying, hot spraying and airless spraying, and either manual or automatic methods are suitable.

The thickness of the base-coat film applied is preferably from 0.5 to 1.5 mils and that of the top-coat from 1 to 3 mils (dry film thickness in each case).

Usually, the top-coat composition will be substantially colourless so that the pigmentation effect due to the base-coat is not signi-

ificantly modified, but it may be desirable in some cases to provide a transparent tinting of the top-coat composition by the use of soluble colourants.

5 The invention is illustrated but not limited by the following Examples, in which parts and percentages are by weight:—

#### Example 1

##### Yellow Metallic Base-Coat

10 The following materials were blended together in the order listed below:—

	parts
Yellow pigment dispersion (Formula A below)	34.00
15 Butylated melamine - form- aldehyde resin (67% solu- tion in <i>n</i> - butanol)	0.70
Carbon black pigment disper- sion (Formula B below)	2.70
20 Cellulose acetate butyrate solution (Formula C below)	19.30
<i>n</i> - Butyl acetate	32.00
Aluminium paste dispersion (Formula D below)	4.20
25 <i>n</i> - Butyl acetate	7.10
	<hr/> 100.00 <hr/>

30 This base-coat had a viscosity of 47 seconds in a British Standard Type B No. 4 efflux cup at 25°C. The resin compositions on a solids basis was as follows:

Acrylic resin	45.5%
M/F resin	19.5%
Cellulose acetate butyrate	35.0%

35 and the pigment to resin solids ratio was 50/100.

##### Formula A

40 The following were ground together in a mill until a sample tested by Hegman gauge showed a degree of dispersion below 5 microns:

	parts
Acrylic resin solution (Formula E below)	22.1
Xylene	38.9
45 Yellow pigment (C.I. Pig- ment Yellow 110)	10.7
<i>n</i> - Butyl acetate	15.2

50 After the grinding period, the following materials were added to reduce the viscosity of the pigment dispersion before emptying the mill:

	parts
Butylated M/F resin (67% solids)	5.4
55 <i>n</i> - Butyl acetate	7.7

##### Formula B

The following were ground together in a mill until a sample tested by Hegman gauge showed a degree of dispersion below 5 microns:

	parts
Acrylic resin solution (Formula E below)	40.85
Xylene	27.45
Carbon black pigment	9.85

After the grinding period the following materials were added to reduce the viscosity of the pigment dispersion before emptying the mill:

	parts
Acrylic resin solution (Formula E below)	19.35
Xylene	2.50

##### Formula C

75 The following mixture was stirred at room temperature until all the solid was dissolved:

	parts
Cellulose acetate butyrate (Cellit BS 800) (ex Bayer, W. Germany) ("Cellit" is a Registered Trade Mark)	20.00
<i>n</i> - Butyl acetate	80.00

##### Formula D

85 The following materials were mixed together in the order given and subjected to slow stirring for a period of four hours:

	parts
Aluminium paste (65% metal)	38.4
Xylene	15.3
Acrylic resin solution (Formula E below)	28.3
Butylated M/F resin (67% solids)	18.0

##### Formula E

95 To a reaction vessel equipped with stirrer, thermometer and reflux condenser were charged 33.98 parts of xylene and 1.81 parts of isobutanol. This mixture was heated until reflux was obtained at 130°C. The following materials were mixed together and added to the vessel at a constant rate over 2½ hours whilst maintaining reflux: methyl meth-  
100 acrylate 21.15 parts, butyl acrylate 13.60 parts, butyl methacrylate 7.60 parts, hydroxy-  
ethyl methacrylate 7.15 parts, acrylic acid  
105 0.50 part, tertiary butyl perbenzoate 0.50 part and xylene 4.05 parts.

After the additions of the above, the vessel was sampled hourly and the product tested for solids content and viscosity. After 2 hours  
110 and 4 hours respectively a further 0.05 part of tertiary butyl perbenzoate was added. After

5 hours the product was cooled and the viscosity reduced by the addition of 9.56 parts of isobutanol. The final resin had a non-volatile content of 50%, viscosity of 4 poise at 25°C, acid value of 12 mgKOH/g. and reduced viscosity (0.5% solution in 95/5 ethylene dichloride/ethanol) of 0.170.

#### Clear Finish

A clear resin solution for use over the above base-coat was prepared by mixing the following materials in the order given:

	parts
Butylated melamine - formaldehyde resin (67% solution in <i>n</i> - butanol)	26.50
2 - ethoxyethyl acetate	3.00
Aliphatic hydrocarbon b.r. 100—120°C	7.50
Acrylic dispersion resin (42% solids) (see Formula F below)	63.00

The viscosity of the clear finish was 75 seconds in a British Standard Type B No. 4 Efflux Cup at 25°C. The finish had a non-volatile content of 44.2% and an acrylic resin/melamine resin ratio of 60/40 on a non-volatile basis.

#### Formula F

A stabiliser precursor was prepared by the condensation of glycidyl methacrylate with a polyester produced by the self-condensation of 12 - hydroxystearic acid to an acid value of 31—34 mg KOH/g. on non-volatile.

This precursor was then copolymerised with methyl methacrylate and glycidyl methacrylate in weight ratios of 49:46:5 in a solvent mixture consisting of 2 parts of ethyl acetate to 1 part of butyl acetate. Further butyl acetate was added at the end of the reaction to give a copolymer solution of 33% non-volatile content.

The above copolymer was converted to a polymeric stabiliser containing double bonds by the following process: 98.782 parts of copolymer solution were mixed with 0.440 part of methacrylic acid, 0.057 part of dimethyl coconut amine and 0.006 part of para tertiary butyl catechol. The mixture was heated at reflux (approximately 111°C) until the acid value was less than 1 mg KOH/g. on non-volatile. 0.683 part of *p* - nitrobenzoic acid and 0.032 part of dimethyl coconut amine were then added and the mixture again held at reflux until the acid value was again reduced to less than 1 mg KOH/g. on non-volatile.

The stabiliser obtained by the above process was used in the preparation of an acrylic polymer dispersion as follows:

Hexane (10.423 parts) and heptane (10.423 parts) were charged to a flask fitted with a stirrer, reflux condenser and thermo-

meter. The mixture was heated to reflux (ca 80°C) and a mixture of methyl methacrylate (1.723 parts), azodiisobutyronitrile (0.129 part), primary octyl mercaptan (0.021 part) and stabiliser solution (0.493 part) were mixed together and added rapidly to the flask. Reflux was maintained for 30 minutes during which time a dispersion of seed particles of polymethyl methacrylate was formed.

The following mixture was then added to the flask over a period of 3 hours: hydroxyethyl acrylate (3.962 parts), methacrylate acid (1.034 parts), styrene (11.874 parts), butyl methacrylate (7.666 parts), methyl methacrylate (5.255 parts), 2 - ethylhexyl acrylate (7.925 parts), stabiliser solution (11.457 parts), primary octyl mercaptan (0.100 part) and azodiisobutyronitrile (0.272 part). Reflux was maintained during the addition of this mixture, the temperature gradually rising to 88°C.

When this addition was complete a mixture of azodiisobutyronitrile (0.382 part) and methyl isobutyl ketone (7.287 parts) was added at an even rate over a period of 3½ hours, reflux being maintained during the addition.

At the end of this stage the flask was cooled to 60°C and the following solvent mixture was added to the flask: White spirit (3.104 parts), hydrocarbon of boiling range 188—212°C, 95% aromatics content, known commercially as Solvesso 150 (3.104 parts) ("Solvesso" is a Registered Trade Mark), iso - propanol (2.340 parts), *n* - butanol (6.399 parts), aliphatic hydrocarbon b.r. 100—120°C (2.422 parts) and hydrocarbon of boiling range 162—180°C, 96% aromatic content, known commercially as Solvesso 100 (2.205 parts).

The resulting product had a non-volatile content of 43.0%, acid value 17.5 mg KOH/g. non-volatile, viscosity 3 poise at 25°C and reduced viscosity in 95/5 ethylene dichloride/ethanol of 0.235 dl/g.

#### Application of Base-Coat and Clear Finish

For application of the above materials the following procedure was followed:

The yellow metallic base-coat was thinned with *n* - butyl acetate until a viscosity of 45 seconds was obtained in a British Standard Type B No. 3 Efflux Cup at 25°C.

The clear finish was thinned with a mixture of aliphatic hydrocarbon b.r. 120—140°C (70 parts), *n* - butyl acetate (20 parts), aliphatic hydrocarbon b.r. 230—240°C (4 parts) and ethylene glycol diacetate (6 parts) until a viscosity of 35 seconds was obtained in a British Standard Type B No. 3 Efflux Cup at 25°C. In this composition, 56% of the total solvents were aliphatic hydrocarbons with no solvent action for the polymer used in the base-coat.

Two single coats of the yellow metallic base-coat thinned as above were applied by spray

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to an undercoated metal panel allowing the first coat to dry for one minute at room temperature before applying the second. After a further two minutes drying at room temperature a single coat of the clear finish was applied by spray. The panel was allowed to air dry for 5 minutes and then baked in an oven for 30 minutes at 130°C. The resulting panel was of high gloss and exhibited an even metallic appearance all over with a desirable degree of "glamour" when examined at different angles to the incident light. The dry film thicknesses obtained by this process were 15 microns (0.6 mils.) of base-coat and 37 microns (1.6 mils.) of clear finish.

#### Example 2

##### Light Blue Metallic Base-Coat

The following materials were blended together in the order listed below:

	parts
20 Butylated melamine - formaldehyde resin (67% solution in <i>n</i> - butanol)	4.45
25 Acrylic resin solution (Formula G below)	13.15
Xylene	7.10
Phthalocyanine blue pigment dispersion (Formula H below)	1.45
30 Cellulose acetate butyrate solution (Formula J below)	27.00
Xylene	10.50
<i>n</i> - Butyl acetate	14.75
35 Aluminium paste dispersion (Formula K below)	17.10
<i>n</i> - Butyl acetate	4.50

This base-coat had a viscosity of 38 seconds in a British Standard Type B No. 4 Efflux Cup at 25°C. The resin composition on a solids basis was as follows:

Acrylic resin	49.0%
M/F resin	21.0%
C.A.B.	30.0%

The pigment to resin solids ratio was 16/100.

##### Formula G

To a reaction vessel equipped with stirrer, thermometer and reflux condenser were charged *n* - butyl acetate (37.86 parts) and methyl ethyl ketone (6.06 parts). This mixture was heated until reflux was obtained (approx. 110°C). The following mixture was then added to the vessel over a period of 3 hours whilst maintaining the batch at reflux: Styrene (12.62 parts), methyl methacrylate (8.58 parts), butyl methacrylate (7.57 parts), butyl acrylate (13.63 parts), hydroxy ethyl methacrylate (6.83 parts), xylene (3.25 parts), acrylic acid (0.58 part), tertiary dodecyl

mercaptan (0.09 part) and di-tertiary butyl peroxide (0.51 part). The mixture was maintained at reflux for a further 7 hours after the monomer addition was complete, an addition of 1.21 parts of an 8.35% solution of benzoyl peroxide in toluene being made after 3 hours and again after 6 hours during this period.

The resin solution was then cooled and was found to have the following characteristics:— 50% non-volatile content, acid value 12.5 mg KOH/g. non-volatile content, acid value 12.5 mg KOH/g. and a reduced viscosity (in 95/5 ethylene dichloride/ethanol) of 0.400.

##### Formula H

The following were ground together in a mill until a sample tested by Hegman gauge showed a degree of dispersion below 5 microns:

	parts
Acrylic resin solution (Formula G above)	42.60
Xylene	32.20
Phthalocyanine blue pigment	9.70

After the grinding period the following materials were added to reduce the viscosity of the pigment dispersion before emptying the mill:

	parts
Acrylic resin solution (Formula G above)	11.70
Xylene	3.80

##### Formula J

The following mixture was stirred at room temperature until all the solid was dissolved:

	parts
Cellulose acetate butyrate EAB 551—0.2 (ex Eastman Kodak U.S.A.)	25.00
<i>n</i> - Butyl acetate	56.25
2 - Ethoxyethyl acetate	18.75

##### Formula K

The following materials were mixed together in the order given and subjected to slow stirring for a period of four hours:

	parts
Aluminium paste (65% metal)	20.00
Xylene	17.00
Acrylic resin solution (Formula G above)	48.00
Butylated M/F resin (67% solids)	15.00

##### Application of Base-Coat and Clear Coat

For application the base-coat above was thinned with butyl acetate to a viscosity of 28

seconds in a British Standard Type B No. 3 Efflux Cup at 25°C. The clear coat was the same as that used in Example 1. The same application method as that described in Example 1 was followed and the same result was obtained, in that a glossy panel of even metallic appearance was obtained. The dry film thickness of the base-coat was 18 microns (0.7 mils.) and that of the clear coat 35 microns (1.4 mils.).

### Example 3

#### Silver Metallic Base-Coat

The following materials were blended together in the order listed below:

15	Butylated melamine - formaldehyde resin (67% solution in <i>n</i> - butanol)	parts
	Aluminium paste dispersion (Formula L below)	3.14
20	Acrylic resin dispersion (42% solids) (Formula F above)	28.60
	Cellulose acetate butyrate solution (Formula J above)	20.00
25	Iso - Propanol	18.10
	<i>n</i> - Butyl acetate	13.60
	Aliphatic hydrocarbon b.r. 100—120°C	9.00
		7.56

30 This base-coat had a viscosity of 38 seconds in a British Standard Type B No. 4 Efflux Cup at 25°C. The resin composition on a solids basis was as follows:

35	Acrylic resin	56%
	M/F resin	14%
	C.A.B.	30%

and the aluminium to resin solids ratio was 50/100.

#### Formula L

40 The following materials were mixed together in the order given and subjected to slow stirring for a period of four hours:

	Aluminium paste (65% metal)	parts
45	<i>n</i> - Butyl acetate	30.0
	Butylated M/F resin (67% solids)	8.6
	Acrylic dispersion resin (Formula F above)	4.7
50	Cellulose acetate butyrate solution (Formula J above)	29.9
		26.8

#### Application of Base-Coat and Clear Coat

For application of the above-coat the composition was thinned with a solvent blend consisting of:

55	<i>n</i> - Butyl acetate	parts
	2 - Ethoxyethyl acetate	50.00
	Acetone	30.00
		20.00

until a viscosity of 32 seconds was obtained in a British Standard Type B No. 3 Efflux Cup at 25°C.

The Application procedure described in Example 1 was then followed, using the thinned base-coat described above followed by the clear finish of Example 1. After stoving a glossy film of even metallic appearance was obtained. The dry film thickness of the base-coat was 15 microns (0.6 mils.) and that of the clear 38 microns (1.5 mils.).

### WHAT WE CLAIM IS:—

1. A process for the application to a substrate surface of a protective and decorative coating which comprises the steps of (i) applying to the surface a base-coat composition comprising a film-forming, optionally thermosetting, acrylic polymer as hereinbefore defined and a cellulose ester both carried in a volatile organic liquid, the cellulose ester constituting from 2% to 70% of the combined weight of the acrylic polymer and the cellulose ester, together with one or more pigments and optionally a heat-curable cross-linking agent for the base-coat polymer, (ii) drying the base-coat so applied without any stoving operation, to a degree sufficient to permit application thereto of the below-described top-coat composition with substantially no intermixing, (iii) applying to the dried base-coat an unpigmented top-coat composition comprising a stable dispersion of a thermosetting acrylic polymer as hereinbefore defined in a volatile organic liquid in which the polymer is insoluble, together with a heat-curable cross-linking agent for the thermosetting polymer, the dispersion being stabilised by means of a copolymer stabiliser containing one polymeric constituent which is capable of becoming associated with the polyester particles and can additionally become covalently linked to the said polymer, and another polymeric constituent of different polarity which is solvatable by the organic liquid medium, and (iv) subjecting the substrate with the applied base-coat and top-coat to heat in order to cure the unpigmented top-coat and, as appropriate, also the base-coat.

2. A process as claimed in Claim 1, wherein the cellulose ester which is employed is cellulose acetate butyrate.

3. A process as claimed in Claim 1 or Claim 2, wherein the cellulose ester constitutes from 20% to 50% of the combined weight of the cellulose ester and the acrylic polymer in the base-coat composition.

4. A process as claimed in any one of Claims 1 to 3, wherein the pigment in the base-coat composition is a metallic pigment.

5. A process as claimed in any one of Claims 1 to 4, wherein the acrylic polymer employed in the base-coat composition is a polymer or copolymer of one or more alkyl esters of acrylic or methacrylic acids.

6. A process as claimed in any one of Claims 1 to 5, wherein the acrylic polymer employed in the base-coat composition is of the thermosetting type.

5 7. A process as claimed in any one of Claims 1 to 6, wherein the acrylic polymer is present in the base-coat composition in a state of stable dispersion in the organic liquid medium of the composition.

10 8. A process as claimed in any one of Claims 1 to 6, wherein the acrylic polymer is present in the base-coat composition in a state of solution in the organic liquid medium of the composition.

15 9. A process as claimed in any one of Claims 1 to 8, wherein the thermosetting acrylic polymer employed in the top-coat composition is a polymer or copolymer of one or more alkyl esters of acrylic or methacrylic acid.

20 10. A process as claimed in any one of Claims 1 to 9, wherein the cross-linking agent used in the top-coat composition and also, where appropriate, in the base-coat composition, is a melamine - formaldehyde condensate in which a substantial proportion of the methylol groups are etherified by reaction with butanol.

11. A process as claimed in any one of Claims 1 to 10, wherein the proportion of cross-linkable acrylic polymer to cross-linking agent in the top-coat composition and also, where appropriate, in the base-coat composition, is from 50:50 to 90:10 by weight of acrylic polymer to cross-linking agent.

12. A process as claimed in Claim 11, wherein the proportion of cross-linkable acrylic polymer to cross-linking agent is from 60:40 to 85:15 by weight.

13. A process as claimed in any one of Claims 1 to 12, wherein the curing of the top-coat composition and also, where appropriate, of the base-coat composition, is carried out by heating the coated substrate at a temperature in the range 100—140°C.

14. A process according to Claim 1 substantially as hereinbefore described, with reference to the foregoing Examples.

15. A substrate surface carrying a protective and decorative coating whenever applied by a process as claimed in any one of Claims 1 to 14.

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